

PATENT COOPERATION TREATY



From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

ISHII, Hisao
AOYAMA & PARTNERS
IMP Building, 3-7, Shiromi 1-chome
Chuo-ku, Osaka-shi, Osaka 540-0001
JAPON

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year) 29.09.2004

Applicant's or agent's file reference
664230

IMPORTANT NOTIFICATION

International application No.
PCT/JP 03/15905

International filing date (day/month/year)
11.12.2003

Priority date (day/month/year)
11.12.2002

Applicant
AMMONO SP. Z O.O.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international
preliminary examining authority:



European Patent Office - P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040 Tx: 31 651 epo nl
Fax: +31 70 340 - 3016

Authorized Officer

Delmon, G

Tel. +31 70 340-2525



PATENT COOPERATION TREATY

PCT

RECEIVED

04 OCT 2004

WIPO

PCT



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 664230	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/JP 03/15905	International filing date (<i>day/month/year</i>) 11.12.2003	Priority date (<i>day/month/year</i>) 11.12.2002
International Patent Classification (IPC) or both national classification and IPC C30B25/02		
Applicant AMMONO SP. Z O.O.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:
- I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the International application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 09.07.2004	Date of completion of this report 29.09.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Cook, S Telephone No. +31 70 340-3372 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/JP 03/15905

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-5, 7-19, 22-24, 27-39	as originally filed
6, 20, 21, 25, 26	received on 14.07.2004 with letter of 09.07.2004

Claims, Pages

40, 43-46	as originally filed
41, 42	received on 14.07.2004 with letter of 09.07.2004

Drawings, Sheets

1/6-6/6	as originally filed
---------	---------------------

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/JP 03/15905

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-29
	No: Claims	
Inventive step (IS)	Yes: Claims	1-29
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-29
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1:** *LIU L ET AL: "Substrates for gallium nitride epitaxy" MATERIALS SCIENCE AND ENGINEERING R: REPORTS, ELSEVIER SEQUOIA S.A., LAUSANNE, CH, vol. 37, no. 3, 30 April 2002 (2002-04-30), pages 61-127, XP004349792 ISSN: 0927-796X*
- D2:** *FR-A-2 796 657 (THOMSON CSF) 26 January 2001 (2001-01-26)*
- D3:** *WO 97/13891 A (GRZEGORY IZABELLA ;KRUKOWSKI STANISDAW (PL); STEPNIEWSKI ROMAN (PL) 17 April 1997 (1997-04-17)*

Novelty

None of the prior art documents cited in the international search report discloses substrates or their process of preparation having those features set out in the independent claims 1 and 23. The present application thus satisfies the criterion set forth in Article 33(2) PCT because the subject matter of claims 1 and 23, along with their dependent claims, is new in respect of prior art defined in the regulations(Rule 64(1)-(3) PCT).

Inventive Step

The application addresses the problem of producing template type substrates of (gallium, aluminium) nitride single crystals for opto-electric applications. Problematic in prior art teachings has been the matter of dislocation density and speed of production. In the document D1 (see p. 112, part 8) gallium nitride itself is said to be the best (template) substrate for gallium nitride epitaxy with lower dislocation density and better control over crystal polarity when compared to heteroepitaxial processes involving template substrates of different materials. In the document D2 gallium nitride bulk crystals are formed from a super-critical ammonia containing solution very similarly to the process of the present application. However, D2 gives no concrete examples and does not suggest that the resulting bulk crystals can be used as a template substrate with the Ga-polar face uppermost for subsequent nitride film epitaxy. D3, considered as the closest prior art, teaches a different method for producing GaN bulk crystals which are used as substrates for subsequent epitaxy. In D3, however, epitaxy is performed on the so-called rough N- polar side and there is no suggestion of using the Ga-polar side to form a template substrate. It is not obvious for the skilled person, on the basis of these teachings, individually or in combination, to arrive at the presently claimed subject matter. The present application therefore satisfies the criterion set forth in Article 33(3) PCT because the subject matter of claims 1- 29 is not obvious and

thus involves an inventive step.

Industrial applicability

The claimed subject matter is considered to be industrially applicable and thus fulfilling the requirements of Article 33(4) PCT.

Further remarks

The application does not fully comply with Article 6 PCT because the claims do not clearly define the matter for which protection is sought and are not fully supported by the description. In particular, it is noted that the description only describes gallium or aluminium nitride as possibilities for the bulk monocrystal nitride and AlGaInN type compositions for the vapour phase epitaxial layer. Given the all embracing scope of the term "nitride" and the multitude of possible compounds with different chemical and physical properties, support in the description is only to be found for the different possibilities described in claims 2, 3, 7 .

Concerning the expression "*containing at least one element of alkali metals*" used throughout the claims, this is not clear since all materials used in one industrial form or another will contain alkali metals albeit at the atomic impurity level. From the description (see page 32), it is understood that the claimed products contain more than 0.1 ppm of alkali metals.

the layer C) is combined at non N-polar face of the layer A1) and N-polar face of the layer C). Therefore, the layer C) of the gallium or aluminum-containing nitride may be prepared on a substrate of the layer A1) by means of MOCVD, HVPE or MBE. In a preferred embodiment, the layer C) can be composed of at least two layers and the first layer C1) is prepared on a substrate of the layer A1) by means of MOCVD or MBE and the second layer C2) can be prepared on the first layer C1) by means of HVPE as shown in Fig.8B.

According to this invention, the first layer C1) can protect the surface of the substrate A) not to be interfered by a HVPE process for the layer C2) and also can avoid diffusion of Alkali metals from the substrate A) to the layer C2). The layer C1) is preferably prepared at a temperature lower than a formation temperature of mono-crystal thereof.

According to this invention, there can be obtained a template type substrate having a dislocation density of $10^6/\text{cm}^2$ or less as well as the value of FWHM of the X-ray rocking curve from (0002) plane less than 80 arcsec.

In the supercritical ammono process, we have discovered that A-axis growth is 4 times or more faster than that of C-axis growth and A-axis growth in the supercritical ammono method makes a dislocation density decreased too much in comparison with C-axis growth in the

dissolution of gallium- or aluminum-containing feedstock. The supercritical ammonia-containing solvent may also contain derivatives of ammonia and/or their mixtures, in particular - hydrazine.

5 **Mineralizer** is a substance delivering one or more types of ions of alkali metals to the supercritical ammonia-containing solvent, supporting dissolution of gallium- or aluminum-containing nitride.

10 Substances containing oxygen-free species causing the weakening of ammono-basic nature of the supercritical solution are selected from the group which includes:

a) compounds AmB_n , where A means H^+ and/or metal, preferably alkali, NH_4^+ , Si, S, P, whereas B means halogens, S, P, and n and m mean corresponding stoichiometric

15 coefficients not lower than 1 and/or

b) groups of species such as:

- S_4N_4 , S_2N_2 , SN, S_4N_2 , $S_{11}N_2$, P_3N_5 , P_4N_6 , PN,

- PN_2^- , PN_3^{4-} , PN_4^{7-} , PN^- , PN^{2-} ,

- $PNCl_2$, $P(NH)_2NH_2$, P_4S_{10} , NP $(SNH_4)_2$, $NPSNH_4SH$, $NP(SH)_2$, PNS,

20 Sulfur or silicon species built in the crystalline lattice of the gallium-containing nitride serve as donors; magnesium, zinc or cadmium are acceptors; dopants such as manganese or chromium in the crystalline gallium nitride lattice provide it with magnetic properties; whereas

25 phosphor atoms are isoelectronic with respect to nitrogen

atoms, and thus they make the energy gap narrower than that in the pure gallium-containing nitride. Those species do not only cause the weakening of ammono-basic nature of the supercritical solvent, but they also modify optical,
5 electrical and magnetic properties of the gallium-containing nitride.

Dissolution of the gallium-containing feedstock is a reversible or irreversible process of formation, through the feedstock, of gallium compounds soluble in the
10 supercritical solvent, for example gallium complexes. Gallium complexes are chemical complex compounds, in which centrally placed gallium atom is surrounded by NH_3^- type ligands or their derivatives, such as NH_2^- , NH^{2-} . Analogical definition for dissolution of the aluminum-containing
15 feedstock applies.

Supercritical ammonia-containing solution means a solution obtained as a result of dissolution of the gallium- or aluminum-containing feedstock in the supercritical ammonia-containing solvent.

20 **Solubility:** Our experiences show that equilibrium may be achieved between the solid, which is gallium- or aluminum-containing nitride, and the supercritical solution at sufficiently high temperature and pressure. Therefore, solubility of gallium- or aluminum-containing nitride may

a primary substrate and susceptible to the lateral overgrowth of crystalline nitrides may be used as a seed. Moreover, a seed having a homoepitaxial surface, exhibiting n-type electrical conductivity, for example doped with Si, may be used. Such seeds can be produced using processes for gallium-containing nitride crystal growth from gaseous phase, such as HVPE or MOCVD, or else MBE. Doping with Si during the growth process at the level of 10^{16} to $10^{21}/\text{cm}^3$ ensures n-type electric conductivity. Moreover, a composite seed may be used and in such seed directly on a primary substrate or on a buffer layer made for example of AlN - a layer made of GaN doped with Si may be deposited. Furthermore, for a particular future use, bulk monocrystals can be grown by the process according to the present invention on homo-seeds having a defined orientation with respect to hexagonal wurzite type crystallographic lattice of the specific Group XIII element(s) nitride, such as C-plane, A-plane or M-plane of the respective nitride.

Spontaneous crystallization from the supersaturated supercritical ammonia-containing solution means any undesirable process of nucleation and growth of the gallium- or aluminum-containing nitride crystals taking place at any site within the autoclave except on the surface of the seed. The definition also includes growth on

the surface of the seed, in which the grown crystal has the orientation different from that of the seed.

Selective crystallization on the seed means the process of crystallization taking place on the surface of the seed in the absence of spontaneous crystallization, but also when spontaneous crystallization occurs in negligible degree. This process is indispensable to obtain bulk mono-crystal and, at the same time, it is one of the elements of this invention.

Temperature and pressure of the reaction: In the examples presented in the specification, temperature profile inside the autoclave was measured with use of an empty autoclave, thus without supercritical ammonia-containing solution. Therefore, these are not real temperatures of the process carried out in supercritical conditions. Pressure was measured directly or calculated on the basis of physico-chemical data of ammonia-containing solvent for the assumed temperature of the process and autoclave volume.

MOCVD Method (Metallo-Organic Chemical Vapor Deposition) means the process of deposition of epitaxial layers from a gaseous phase, in which ammonia and metallo-organic gallium compounds are used as reagents in the case of gallium nitride.

HVPE Method (Halide Vapor Phase Epitaxy) means the process of deposition of epitaxial layers from a gaseous phase, in

B) is composed of at least two layers and the first layer B1) is prepared on a substrate having the layer A) by means of MOCVD or MBE and the second layer B2) is prepared on the first layer B1) by means of HVPE.

5 6. A template type substrate used for opto-electric or electrical devices according to claim 1, wherein the layer A) of bulk mono-crystal nitride is prepared on a seed having the layer B) by crystallization of nitride in a supercritical ammonium solution containing at least one
10 element of alkali metals.

7. A template type substrate used for opto-electric or electrical devices according to claim 1, which further comprises C) a layer of gallium or aluminum-containing nitride grown by means of vapor phase epitaxy growth
15 wherein the layer A) of bulk mono-crystal nitride containing at least one element of alkali metals (Group I, IUPAC 1989) is prepared on both of non N-polar face and N-polar face of the seed layer B) as layers A1) and A2) and the layer C) is combined at non N-polar face of the layer
20 A1) and N-polar face of the layer C).

8.(amended) A template type substrate used for opto-electric or electrical devices according to claim 7, wherein the layer C) of the gallium or aluminum-containing nitride is prepared on a substrate of the layer A1) by
25 means of MOCVD, HVPE or MBE.

9.(amended) A template type substrate used for opto-electric or electrical devices according to claim 7, wherein the layer C) is composed of at least two layers and the first layer C1) is prepared on a substrate of the layer A1) by means of MOCVD or MBE and the second layer C2) is prepared on the first layer C1) by means of HVPE.

10. A template type substrate for opto-electric or electrical devices according to claim 1, wherein the substrate contains chloride and has a main surface substantially consisting of Ga-polar face.

11. A template type substrate used for opto-electric or electrical devices according to claim 1, wherein the substrate has a dislocation density of $10^6/\text{cm}^2$ or less.

12. A template type substrate used for opto-electric or electrical devices according to claim 1, wherein the layer A) or the layers A1) and A2) are of bulk mono-crystal nitride prepared by crystallization of nitride in a supercritical ammonium solution containing at least one element of alkali metals.

13. A template type substrate used for opto-electric or electrical devices according to claim 1, wherein the layer A), having a pair of C-plane surfaces and a diameter of 1 inch or more, is prepared by A-axis direction growth of bulk mono-crystal nitride in a supercritical ammonium solution containing at least one element of alkali metals.